United States Patent

[11] 3,619,184

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[54] **BALANCED TITANIUM ALLOY**
4 Claims, 1 Drawing Fig.

[52] U.S. Cl. 75/175.5
[51] Int. Cl. C22c 15/00
[50] Field of Search 75/175.5; 148/32, 32.5, 133

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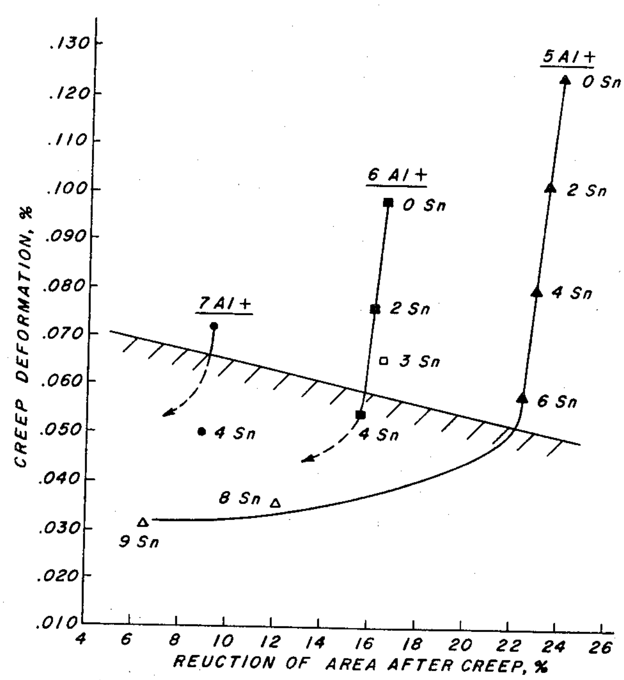
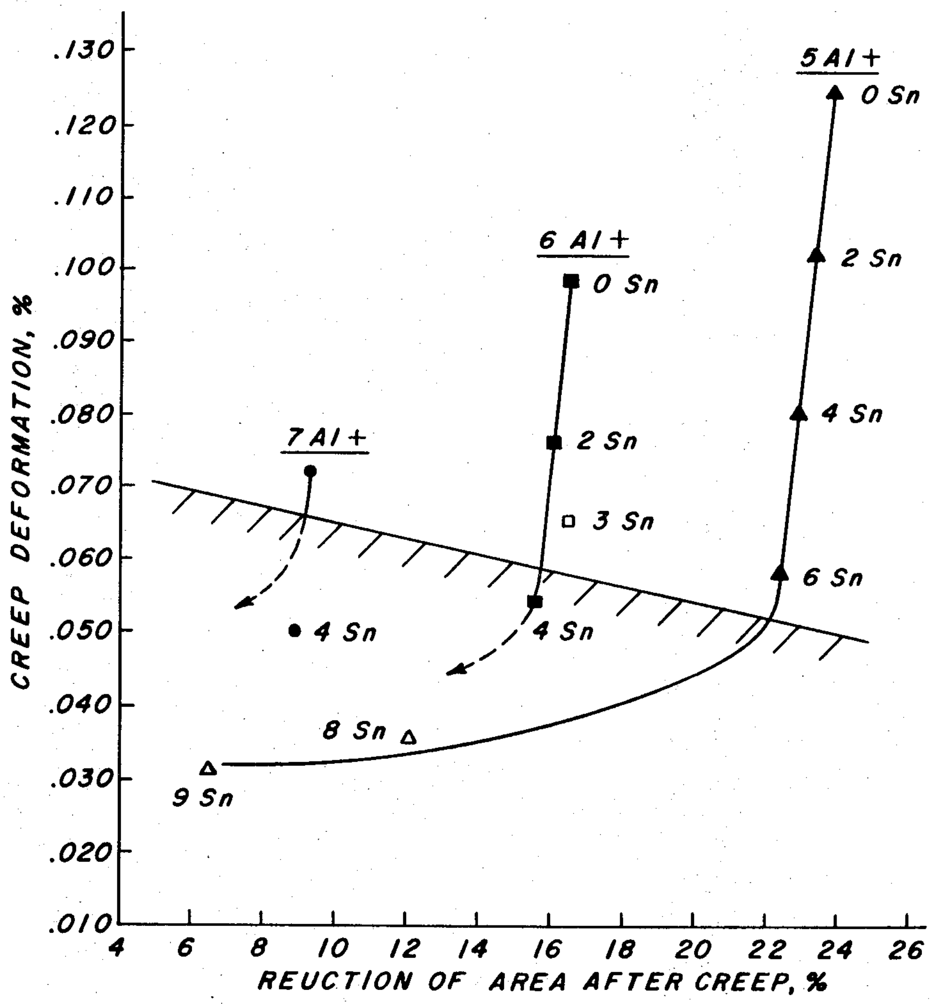
ABSTRACT: A titanium alloy containing aluminum, zirconium, silicon, at least one stabilizer from the group consisting of molybdenum, columbium, tantalum, vanadium and tungsten and which may also contain tin, all balanced in accordance with prescribed relationships.





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BALANCED TITANIUM ALLOY

Historically, one of the main attributes of titanium and alloys of titanium has been the excellent strength-to-weight ratio of these materials for applications involving exposure to moderately high temperatures. This property has resulted in extensive use of titanium alloys in the manufacture of articles subject to exposure to temperatures of up to 850° F. However, the need for higher performance, in the aircraft industry for example, has necessitated the development of new and improved alloys capable of maintaining their desirable strength-to-weight ratio at temperatures as high as 1,000° F. Material with this capability is particularly desirable in the manufacture of aircraft engine components.

The natural crystallographic grouping of titanium and its alloys involves three categories divided according to the predominant phase or phases in their microstructure. These groups are alpha, beta and mixed alpha and beta phases. In pure titanium, the alpha phase which is characterized by a hexagonal, close-packed crystallographic structure is stable from room temperature to approximately 1,620° F. The beta phase of pure titanium has a body-centered cubic structure and is stable from approximately 1,620° F. to the melting point of about 3,035° F.

The hexagonal, close-packed allotrope of titanium, i.e. the alpha phase, demonstrates excellent resistance to creep. Solid solution strengthening of the alpha phase by the addition of aluminum, tin and zirconium has resulted in alloys with still better resistance to creep deformation. However, further improvements by the addition of such alpha stabilizers is restricted due to poor thermal stability of compositions containing too great a quantity of such elements as manifested by lower ductility after creep exposure. The present invention provides a balanced titanium alloy composition which possesses improved creep strength without undue sacrifice of thermal stability or ductility after creep exposure.

In accordance with the invention there is provided a titanium alloy consisting essentially of 4.0 to 7.8 percent aluminum, up to 12.0 percent tin, at least 0.3 percent zirconium, traces to 0.5 percent silicon and at least one stabilizer from the group consisting of molybdenum, columbium, tantalum, vanadium and tungsten, the quantity of aluminum, tin and zirconium complying with the equation:

$$\text{Percent aluminum} + \frac{\text{Percent tin}}{3} + \frac{\text{Percent zirconium}}{6} \leq 8$$

and the quantity of stabilizer being in accordance with the equation:

$$\%Mo+0.5(\%Cb)+0.2(\%Ta)+c0.75(\%V)+0.5(\%W)=0.1 \text{ to } 1.5\%,$$

and the balance essentially titanium and usual impurities.

A preferred alloy in accordance with the invention contains 4.0 to 7.0 percent aluminum, 0.3 to 7.0 percent zirconium, 2.0 to 8.0 percent tin, 0.1 to 0.35 percent silicon and 0.1 to 1.2 percent of at least one stabilizer from the group consisting of molybdenum, columbium, tantalum, vanadium and tungsten. Optimum properties have been found to be associated with a composition within the melting range 4.7 to 5.3 percent aluminum, 5.5 to 6.5 percent tin, 0.5 to 2.5 percent zirconium, 0.4 to 1.1 percent molybdenum, 0.2 to 0.3 percent silicon, more specifically having the nominal composition of 5.0 percent aluminum, 6.0 percent tin, 2.0 percent zirconium, 0.8 percent molybdenum and 0.25 percent silicon.

It has been demonstrated that considerable improvement in properties can be accomplished in certain alloy systems by using dispersed phases. In accordance with the present invention, there is utilized the fact that silicon additions are potentially useful in strengthening titanium alloys by the formation of dispersible compounds. The addition of silicon results in a secondary silicide phase which impedes dislocation movement and thus improves creep strength. It has been found, however, in accordance with the invention, that the addition of silicon to a carefully formulated base composition with critically balanced alpha- and beta-stabilizing elements can maximize the improvement in creep strength with acceptable thermal stability and ductility following creep exposure. It is essential, however, that the components of the alloy be critically controlled to achieve these results. Thus, for example, alloys in accordance with the invention contain 4.0 to 7.8 percent aluminum. If the upper aluminum limit is exceeded, the alloy becomes thermally unstable; similarly, a minimum of 4.0 percent aluminum is necessary to achieve acceptable mechanical properties. Zirconium has been found to enhance the creep-strengthening effect of silicon and at least 0.3 percent zirconium is necessary for this purpose. Zirconium-containing alloys result in the formation of a complex compound of titanium, zirconium and silicon instead of normal titanium silicide which would form in the absence of zirconium. Some silicon is, of course, necessary for creep strengthening. However, amounts in excess of 0.5 percent are avoided to avoid ductility problems. Tin may act as a replacement for aluminum, at least in part, and is desirable, but not absolutely necessary, since it further assists in assuring thermal stability. However, over 12.0 percent tin increases the tendency toward thermal instability. A critically controlled quantity of at least one stabilizer from the group consisting of molybdenum, columbium, tantalum, vanadium and tungsten is necessary in balancing the alpha-stabilizing components to assure additional high-temperature strength while imparting thermal stability which is particularly beneficial for alloys processed or heat treated above the beta transus. However, a discovery in accordance with the invention is that the addition of the stabilizers must not exceed the alpha-solubility limit for the particular stabilizer. If the alpha-solubility is exceeded, some beta phase may form that would result in a significant less of strength which may be accompanied by a loss of high-temperature stability as well.

The following examples will serve to further illustrate titanium alloys in accordance with the invention.

A series of alloys of varying compositions were prepared and samples thereof examined for tensile strength, yield strength, elongation and reduction in area, before and after creep exposure. The amount of deformation due to creep exposure was also determined. Results of these tests and the compositions involved are reported in table I. The first sample (Alloy 1) is an alpha-matrix alloy which shows creep deformation of 0.23 percent. The addition of 0.8 percent molybdenum, shown in table I as Alloy No. 2, results in an improvement in creep strength as indicated by a lower percent deformation. The addition of silicon to this base, seen in Alloy No. 3, also improves the creep strength but the alloy is brittle after creep exposure. However, the combined addition of molybdenum and silicon, Alloy No. 4, results in significantly better creep strength (0.03 percent) than both of the alloys with similar individual additions, i.e. Alloy Nos. 2 and 3. Moreover, Alloy No. 4 possesses good tensile ductility after creep exposure while Alloy No. 3 is brittle.

TABLE I

Alloy	Composition, wt. percent	Before creep					After creep			
		UTS, K s.i.	YS, K s.i.	El, percent	RA, percent	Def.[1], percent	UTS, K s.i.	YS, K s.i.	El, percent	RA, percent
1	Ti-6Al-3Sn-3Zr	131	114	11	26	.23	127	120	8	12
2	Ti-6Al-3Sn-3Zr-.8Mo	147	130	10	23	.14	148	123	8	15
3	Ti-6Al-3Sn-3Zr-.3Si	144	128	11	24	.08	Broke in shoulder			
4	Ti-6Al-3Sn-3Zr-.3Si-.8Mo	147	128	11	22	.04	146	130	13	15
		157	141	8	18	.01	155	140	8	14
		156	141	10	18	.03	156	142	12	17
5	Ti-6Al-3Sn-3Zr-.15Si-.8Mo	145	131	11	24	.03	150	139	12	20
		148	131	10	20	.04	145	132	12	20
6	Ti-6Al-3Sn-3Zr-.3Si-.4Mo	155	144	10	21	.03	156	146	10	16
7	Ti-6Al-3Sn-3Zr-.3Si-1.2Mo	156	134	11	22	.09	159	141	13	16
8	Ti-6Al-2Sn-4Zr-.2Si-2.0Mo	158	139	10	15	.15	156	143	9	11

[1] Creep deformation after 950° F.–45 K s.i.–96 hrs.

The amounts of molybdenum and silicon added to the alloy are important in optimizing the creep strength with post creep tensile ductility. Thus, the creep strength of Alloy No. 5 in table I compared with Alloy Nos. 2 and 3 indicates that the combination of beta stabilizers plus silicon, e.g. molybdenum plus silicon, even at lower silicon contents, is superior. The influence of the stabilizers, in this case molybdenum, is shown by comparing Alloy No. 3 with Alloy Nos. 4, 6 and 7 7 in table I. The slight addition of 0.4 percent molybdenum is sufficient to impart improved creep strength. With 0.8 percent molybdenum, the excellent creep strength is still maintained. However, at the 1.2 percent molybdenum level a moderate decrease in creep strength occurs. Higher molybdenum contents, as illustrated by Alloy No. 8, further reduce the creep strength. The improvement in creep strength is believed to be limited to the solubility of the beta stabilizer, e.g. molybdenum, in the alpha phase. The maximum creep strength should occur at maximum solubility which is about 0.8 percent for molybdenum. Other beta stabilizers added in amounts within the alpha-solubility limit also improve creep strength. These limits may be exceeded to some extent, within the purview of the invention, but at some loss of creep strength. Actual alpha-solubility limits are: tantalum—up to 7.5 percent; columbium—up to 3.0 percent; molybdenum—up to 0.8 percent; vanadium—up to 1.5 percent; and tungsten—up to 1.0 percent.

A series of examples shown in table II illustrate improvements for vanadium, columbium and tungsten additions. Similarly, addition of tantalum, up to about 7.5 percent, will be effective.

Alloy Nos. 5 through 8 in table II illustrate the beneficial effects of tungsten while alloy No. 9 contains both molybdenum and tungsten. Alloy No. 10 contains silicon in addition to tungsten and molybdenum, and represents the alloy with the best combination of properties in this particular system. Alloy No. 11 contains both columbium and molybdenum in addition to silicon.

Additional compositions described in table III further illustrate the importance of adjusting the beta stabilizer content. As is shown by comparing Alloy Nos. 1, 2 and 3, the beneficial influence of silicon is clearly related to the creep strength. However, post creep ductility is improved by the combination of beta stabilizers and silicon.

The importance of zirconium in the alloy system in accordance with the invention is shown in the examples in table IV. With zirconium, higher creep resistance is obtained. The zirconium addition results in the formation of a complex $(TiZr)_5Si_3$ compound which benefits creep resistance. Thus, a minimum quantity of zirconium is necessary to improve creep strength.

TABLE II

Alloy	Composition	Before creep: UTS, K s.i.	YS, K s.i.	El, percent	RA, percent	Def.[1], percent	After creep: UTS, K s.i.	YS, K s.i.	El, percent	RA, percent
1	Ti-6Al-3Sn-3Zr-.3Si	144	128	11	24	.08	Broke in shoulder			
2	Ti-6Al-3Sn-3Zr-.3Si-0.8Mo	157	141	8	18	.01	155	140	8	1[illegible]
3	Ti-6Al-3Sn-3Zr-.3Si-1.5V	153	134	7	17	.02	151	136	7	1[illegible]
4	Ti-6Al-3Sn-3Zr-.3Si-1.0W	152	137	9	19	.03	154	146	3	[illegible]
5	Ti-6Al-3Sn-3Zr	131	114	11	26	.23	127	120	8	1[illegible]
6	Ti-6Al-3Sn-3Zr+0.5W	131	115	14	30	.29	135	129	14	2[illegible]
7	Ti-6Al-3Sn-3Zr+1.0W	143	132	11	22	.13	145	139	7	1[illegible]
8	Ti-6Al-3Sn-3Zr-1.5W	146	133	11	27	.11	149	139	8	1[illegible]
9	Ti-6Al-3Sn-3Zr-1.0W+0.8Mo	154	134	11	20	.13	153	139	12	2[illegible]
10	Ti-6Al-3Sn-3Zr-1.0W+0.8Mo+.3Si	160	135	11	15	.00	162	140	10	1[illegible]
11	Ti-6Al-3Sn-3Zr-0.8Mo-.3Si-1.3Cb	161	142	10	13	[2] .08	157	140	8	[illegible]

[1] Creep deformation after 950° F.-45 K s.i.-96 hrs. [2] Creep deformation after 1,000° F.-45 K s.i.-96 hrs.

TABLE III

Alloy	Composition, wt. percent: Al	Sn	Zr	Mo	Si	Before creep: UTS, K s.i.	YS, K s.i.	El, percent	RA, percent	Def.[1], percent	After creep: UTS, K s.i.	YS, K s.i.	El, percent	RA, percent
1	6	3	3	0.8	.30	156	141	10	18	.03	156	142	12	1[illegible]
2	5	1	1	0.4	.20	133	120	11	27	.16	134	125	10	2[illegible]
3	7	5	1	1.2	.40	153	130	11	17	.04	150	132	5	1[illegible]
4	7	1	5	1.2	.20	161	138	10	14	.04	162	144	3	[illegible]
5	5	5	5	0.4	.20	144	128	9	26	.04	144	130	11	1[illegible]
6	5	5	1	1.2	.40	158	134	10	22	.05	158	137	11	2[illegible]
7	5	1	5	1.2	.40	157	134	8	13	.04	155	133	8	1[illegible]
8	7	5	5	0.4	.40	149	144	1	2	.06	Brittle			
9	6	3	3	0.8	.15	148	131	10	20	.04	145	132	12	2[illegible]
10	4	12	0	1.2	.30	151	131	10	17	.50	154	138	7	1[illegible]
11	5	9	0	1.2	.30	159	135	12	17	.12	153	134	12	1[illegible]
12	5	9	2	0.8	.30	158	135	9	17	.04	160	143	2	[illegible]
13	5	8	2	0.8	.15					.04	152	138	13	1[illegible]
14	5	8	2	0.8	.30					.02	162	146	8	1[illegible]
15	5	9	0	0	0	131	116	18	32	1.10	128	120	17	3[illegible]
16	5	9	0	1.2	0	150	128	12	19	.30	149	131	13	2[illegible]
17	6	3	3	0	0	131	114	11	26	.23	127	120	8	1[illegible]
18	6	3	3	0	.3	144	128	11	24	.08	Brittle			
19	6	3	3	0	[2] .5	155	142	11	26	.19	156	145	4	[illegible]
20	6	0	6	0	[2] 0	129	117	13	31	.70	134	126	14	2[illegible]
21	6	0	6	0	[2] .3	144	132	10	20	.13	138	130	10	1[illegible]
22	5	5	5	0	0	129	113	12	29	.26	130	121	12	2[illegible]
23	5	5	5	0	.3	143	127	10	21	.14	143	131	13	1[illegible]
24	6	3	3	1.2	.3	156	134	11	22	.09	159	141	13	1[illegible]
25	6	3	3	0.4	.3	155	144	10	21	.03	156	146	10	1[illegible]

[1] Creep deformation after 950° F.-45 K s.i.-96 hrs.
[2] $\alpha+\beta$ anneal.

TABLE IV

Alloy	Composition, wt. percent	Before creep: UTS, K s.i.	YS, K s.i.	El, Percent	RA, Percent	Def.[1], Percent	After creep: UTS, K s.i.	YS, K s.i.	El, Percent	RA, Percent
1	Ti-5Al-9Sn-1.2Mo-O.3Si	160	135	12	17	.12	153	135	12	18
2	Ti-5Al-9Sn-O.8Mo-O.3Si-2Zr	159	135	9	17	.02	160	143	3	6

[1] Creep deformation after 950° F.-45 K s.i.-96 Hrs.

It has been further determined that optimum creep strength is achieved by beta processing or heat treatment, and in this connection, the balanced composition of the invention is a particular advance over present commercially available materials. However, optimum yield strength in titanium alloys of the type described is developed by processing, e.g. heat treating, in such a manner so as to avoid the formation of a transformed beta structure. A typical process to develop optimum yield strength involves (1) working to an end temperature below the beta transus temperature or (2) working to an end temperature below the beta transus temperature plus a heat treatment below that temperature.

As indicated previously, balancing of the elements in the alloy must be carefully controlled to achieve maximum benefits from the invention. Various possibilites exist, however, to select particular optimum compositions for specific purposes. For very severe applications requiring creep deformation of less than 0.1 percent together with high thermal stability, i.e. demonstrating a greater than 10 percent reduction in area upon creep exposure, the compositions should be adjusted, within the limits described above, in a particular manner. It has been determined that adjustment of the aluminum, tin, zirconium, silicon and beta stabilizer contents so as to comply with certain hereinafter described creep and stability equations will result in alloys of a high order of creep resistance and thermal stability. Equations useful for this purpose are:

A. Creep Resistance: (Permanent deformation after creep exposure X100)

$$10 \geq 36-2.6(\%Al)-1.1(\%Sn)-0.7(\%Zr)-27(\%Si)-3(Mo_e);$$

B. Stability: (Reduction in area after creep exposure)

$$10 \leq 70-7.2(\%Al)-.25(\%Sn)-1.5(\%Zr)-27.5(\%Si)-0(\%Mo_e).$$

The symbol Mo_e in the above equations refers to molybdenum content or molybdenum equivalency of other stabilizers, i.e. columbium, tantalum, vanadium and tungsten. Molybdenum equivalency is expressed by the equation:

$$\%Mo+0.5(\%Cb)+0.2(\%Ta)+0.75(\%V)+0.5(\%W)=0.1 \text{ to } 1.5\%$$

Creep and stability according to the equations A and B above are determined by testing specimens at 950° F, under 45 k.s.i. load for 96 hours. Reduction in area (RA) is obtained by tensile testing creep specimens after creep exposure with no further preparation of the specimen. Until the present invention, no commercial alloys have been available which met the above requirements of creep resistance and stability.

A graphic illustration of the effects described in table III is shown in the accompanying drawing. In the drawing, the creep deformation of a series of compositions is plotted against the percent reduction of area after creep with particular emphasis with respect to aluminum and tin on creep strength and thermal stability. The graph is related to a base composition of Ti-XAl-YSn-2Zr-0.8Mo-0.25Si based upon an instability threshold of less than 8 where the aluminum, tin and zirconium, i.e. the alpha stabilizers, are related by the equation:

$$\%Al+\frac{\%Sn}{3}+\frac{\%Zr}{6}\leq 7.5\%$$

In the graph, the sloping line represents the tin content for different aluminum levels at which the loss of ductility is disproportionately greater with increase in creep strength, that is, the point at which the equations discussed above are no longer applicable.

It is apparent from the above that various changes and modifications may be made without departing from the invention. Accordingly, the scope of the invention should be limited only by the appended claims wherein what is claimed is:

1. A titanium-base alloy consisting essentially of about 4.7 to 5.3 percent aluminum, 5.5 to 6.5 percent tin, 0.5 to 2.5 percent zirconium, 0.4 to 1.1 percent molybdenum, 0.2 to 0.3 percent silicon, and the balance titanium and incidental impurities, said alloy being characterized by improved creep strength without undue sacrifice of thermal stability or ductility after creep exposure.

2. A titanium alloy in accordance with claim 1 containing 5.0 percent aluminum, 6.0 percent tin, 2.0 percent zirconium, 0.8 percent molybdenum and 0.25 percent silicon.

3. A titanium alloy in accordance with claim 1 additionally containing 0.53 to 1.33 percent vanadium.

4. A titanium alloy in accordance with claim 1 additionally containing 0.8 to 2.0 percent tungsten

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,619,184 Dated November 9, 1971

Inventor(s) Howard B. Bomberger, Jr., et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 51, before "0.75" delete "c". Column 2, line 43, "less" should read -- loss -- . Column 3, line 8, delete the second "7". Column 4, Table II, the last column should read -- 14
15
7
12
22
12
12
21
11
9 --;

and the last column of Table III should read -- 17
27
10
7
19
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23

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,619,184 Dated November 9, 1971

Inventor(s) Howard B. Bomberger, Jr., et al - 2 -

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

19
16
16 -- .

Column 5, line 30, "S1" should read -- Si -- and before "MOe" insert -- % -- ; line 38, before "0.75" delete "c".

Signed and sealed this 14th day of November 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents